Identification of Copper(II)–Lactate Complexes in Cu_2O Electrodeposition Baths: Deprotonation of the α-Hydroxyl Group in Highly Concentrated Alkaline Solution

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Unveiling dissolved species in electrodeposition baths helps our understanding of electrodeposition behavior, such as growth orientation. A highly concentrated aqueous alkaline copper(II)–lactate solution is used for the electrodeposition of copper(I) oxide (Cu_2O) thin films with <111> orientations; the semiconductor properties of these films facilitate their use in solar-cell materials, photocathodes, and photocatalysts. However, the dissolved species, presumably copper(II)–lactate complexes, cannot be deduced on the basis of known thermodynamic data, and have not been convincingly determined yet. In this work, we determine these cupric complexes by pH titration, ultraviolet–visible spectroscopy, and electrospray-ionization mass spectrometry (ESI-MS), including probe-ESI-MS (PESI-MS). Using PESI-MS, we successfully analyzed a highly concentrated solution without sample dilution. The determined complexes are $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$, where the $H_{-1}L^{2-}$ ($CH_3CH(O^-)COO^-$) is a lactate ion with a deprotonated α-hydroxyl group. As far as we know, this is the first direct experimental observation of $H_{-1}L^{2-}$ ions in a highly concentrated aqueous alkaline copper(II)–lactate solution. We also propose that $H_{-1}L^{2-}$ is stabilized by the high concentration and through coordination to copper(II) ions.

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Cuprous oxide (Cu_2O) is a p-type semiconductor that is inexpensive and of low toxicity. Cu_2O thin films are attracting increasing attention as solar-cell materials,[1–5] photocathodes,[6–9] and photocatalysts[10–12] for, for example, water splitting. Among thin-film fabrication methods, electrodeposition from an aqueous solution has advantages over conventional methods, such as chemical vapor deposition, because of its low cost and low environmental burden. Moreover, it is easy to obtain cubic Cu_2O with the preferential <111> orientation by tuning the pH of the electrodeposition bath;[13–17] this orientation relaxes lattice misfit with hexagonal ZnO, which is favorable for Cu_2O–ZnO solar cells.

Since the pioneering work of Rakhshani et al.,[13] highly concentrated aqueous alkaline solutions have commonly been used for Cu_2O electrodeposition;[13–16] these solutions contain 0.4 M of a copper(II) salt and 3.0 M lactic acid (HL; $CH_3CH(OH)COOH$) as the complexing agent, and the pH is adjusted to be in the 9.0–12.5 range.[13–16] The crystal orientation of the electrodeposited Cu_2O is pH dependent; i.e. it is <100> at pH values of 9.0 and 9.5, and <111> at pH values of 12.0 and 12.5.[13–17] The pH dependence of the crystal orientation during Cu_2O electrodeposition may be ascribable to changes in the dissolved copper(II)–lactate complexes.[6,15,16]

Unfortunately, to the best of our knowledge, there are no available thermodynamic data for these copper(II)–lactate complexes under these alkaline conditions, especially for such concentrated solutions. Two previous reports have indicated the presence of dissolved copper(II)–lactate complexes in such concentrated alkaline solutions; Leopold et al. assumed that the copper(II)–lactate complexes are $Cu(H_{-1}L)_2^{2-}$ and $Cu(H_{-1}L)_2(OH)^{3-}$ ($H_{-1}L^{2-} = CH_3CH(O^-)COO^-$, the lactate ion bearing a deprotonated α-hydroxyl group) based on a pH-titration experiment at pH > 8, and by analogy with the alkaline copper(II)–tartrate system,[18] while Achilli et al. proposed CuL_4^{2-} on the basis of energy-dispersive X-ray absorption spectroscopy (EDXAS), where they assumed that L^- functions unusually as a monodentate ligand.[19] These different results leave the copper(II)–lactate complexes in these Cu_2O-electrodeposition baths open to question; consequently, other direct information is required.

In this study, we identified the copper(II)–lactate complexes in Cu_2O electrodeposition baths. Highly concentrated aqueous solutions were investigated using unconventional pH titration over the full pH range, ultraviolet–visible (UV-Vis) spectroscopy, electrospray-ionization mass spectrometry (ESI-MS), and probe-ESI-MS (PESI-MS). PESI-MS has been successfully used to analyze a variety of real-world biological samples without any special pretreatment, such as electrolyte dilution.[20,21] This is the first time that PESI-MS has been used to analyze electrodeposition baths. We obtained clear mass spectra that revealed the dissolved species. We conclude that the unknown copper(II)–lactate complexes are $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ (see Figure 1). As far as we know, this is the first direct experimental observation of $H_{-1}L^{2-}$ ions coordinated to copper(II) ions.

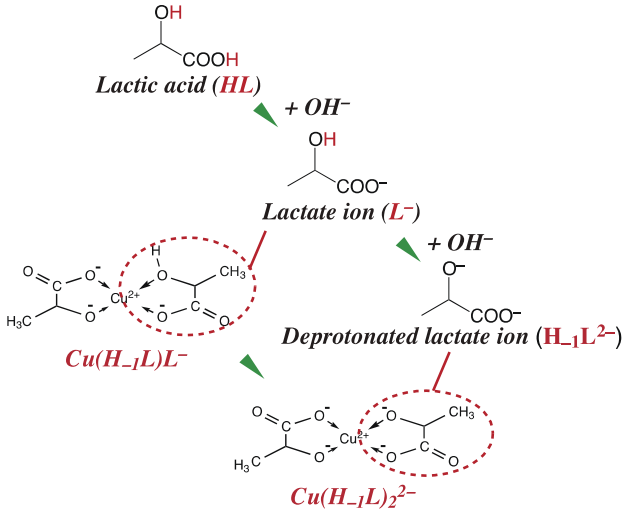

Figure 1. Structures of lactic acid (HL), lactate ion (L^-), deprotonated lactate ion ($H_{-1}L^{2-}$), and the proposed $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ copper(II) complexes, where HL was deprotonated stepwise to form the L^- and $H_{-1}L^{2-}$ ligands.

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Experimental

pH titration.—We conducted two kinds of pH titration, which we refer to as the "traditional pH titration" and the "revised pH titration" methods, as detailed below.

Traditional pH titration.—This titration was conducted by a traditional method using a beaker with the analyte and a burette with the titrant. A 50 mL 0.4 M copper(II)/3.0 M lactate solution (the analyte) was prepared by stirring 0.02 mol (7.49 g) $Cu(ClO_4)_2 \cdot 6H_2O$ (99%, Nacalai Tesque) and 0.15 mol (12.5 mL) 91.1% HL (Nacalai Tesque) in deionized water. A 10 M standard NaOH aqueous solution (Nacalai Tesque) was used as the titrant. We used a piston burette (APB-610; KEM Kyoto) to conduct this titration, where pH was measured using a pH meter (HORIBA D−51; HORIBA) with a glass electrode (HORIBA 9615−10D; HORIBA) at 25°C. To avoid any alkaline error, the glass electrode was successively washed before each use with 1 M hydrochloric acid for 1 h and an aqueous 10% thiourea/1% HCl solution for 1 h. The pH scale was calibrated with commercially available pH standard solutions.

Revised pH titration.—Thirty sets of 15 mL solutions of 0.4 M copper(II)/3.0 M lactate were prepared as analytes. Instead of the consecutive addition of NaOH using a burette, thirty different known amounts of solid NaOH (97%, Nacalai Tesque) (Table I) were added to adjust the pH of each sample, after which these samples were stored in 20-mL airtight screw tubes for 1 week to complete the complexation process. The pH of each sample was then measured at 25°C using the pH meter with the glass electrode, which had been carefully washed and calibrated by the procedure described above.

ESI-MS/PESI-MS.—As the analyte for ESI-MS/PESI-MS, copper(II) lactate dihydrate ($CuL_2 \cdot 2H_2O$) was selected as the copper(II) source, instead of $Cu(ClO_4)_2 \cdot 6H_2O$, in order to minimize and simplify the kinds of counter anions present in solution. A 50 mL solution of 0.4 M copper(II) and 3.0 M lactate was prepared by mixing 0.02 mol (5.73 g) $CuL_2 \cdot 2H_2O$ (97%, Mitsuwa's Pure Chemicals) and 0.11 mol (9.00 mL) of 91.1% HL in deionized water, after which the pH was adjusted by the addition of NaOH. The analyte for ESI-MS was diluted 1000-fold with deionized water, while that for PESI-MS was left undiluted.

Table I. Amounts of added NaOH.

Number	NaOH/g	c_{NaOH}/M
1	0.00	0.00
2	0.20	0.33
3	0.39	0.65
4	0.59	0.98
5	0.78	1.30
6	1.00	1.67
7	1.20	2.00
8	1.40	2.33
9	1.59	2.65
10	1.80	3.00
11	1.83	3.05
12	1.87	3.10
13	1.89	3.15
14	1.91	3.19
15	1.95	3.25
16	1.99	3.30
17	2.01	3.35
18	2.04	3.40
19	2.07	3.45
20	2.10	3.50
21	2.13	3.55
22	2.16	3.60
23	2.19	3.65
24	2.22	3.70
25	2.25	3.75
26	2.28	3.80
27	2.34	3.90
28	2.40	4.00
29	2.46	4.10
30	2.52	4.20

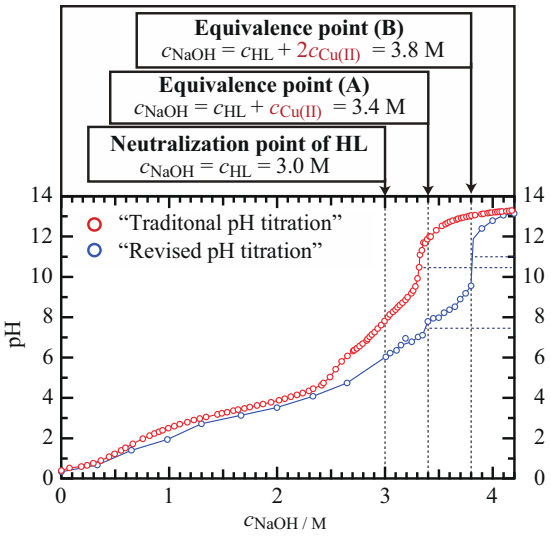

Figure 2. Titration curves for aqueous 0.4 M copper(II)–3.0 M lactate solution with added NaOH (see text for details). Dashed lines indicate neutralization and equivalence points.

UV-Vis spectroscopy.—Several samples of the analyte for the "revised pH titration" were also used for these measurements. Since the optical density of each sample solution was high, a quartz cell with a short optical path length (1 mm) was used for these experimental measurement, with the absorbance data multiplied by ten in order to produce data equivalent to that usually generated with an optical path length of 1 cm.

Results and Discussion

pH titration.—We determined the stoichiometry of the copper(II)–lactate complexes by titration. Figure 2 shows the two pH-titration curves obtained by the "traditional pH titration" and "revised pH titration" methods, as described above. The volume of the analyte for "traditional pH titration" was increased from 50 mL to approximately 70 mL after titration, while the volume change of analyte (15 mL) in "revised pH titration" is negligible. To compare the results of two pH titrations easily with two different volume changes of analytes, the NaOH consumed was recalculated as analytical concentration c_{NaOH} in Figure 2. Note that the initial pH of the titrant was 0.3, indicating that the solution contains copper(II) aquo ions and free lactic acid, HL.

When the added NaOH concentration reached 3.0 M, i.e. $c_{NaOH} = c_{HL} = 3.0$ M, during the "traditional pH titration", all HL molecules were consumed to achieve neutrality by the reaction: $HL + OH^- \rightarrow L^- + H_2O$. On the basis of the stability constants of copper(II)–lactate complexes[22] reported to date (see Table II), copper(II) ions are completely complexed with lactates up to the point of neutralization; i.e., $Cu^{2+} + nL^- = CuL_n^{(n-2)-}$ (n = 1–3), as discussed later. An equivalence point is observed when the NaOH concentration ($c_{NaOH} = c_{HL} + 0.75c_{Cu(II)}$) was approximately 3.3 M, indicating that OH^- reacted further with complexed copper(II) species in a Cu(II):OH^- molar ratio of about 1:0.75, which appears to be the same value as that observed by Leopold et al.[18] The pH at the equivalence point was 10.4; however, the pH following each drop of titrant was found to be unstable, and was observed to decrease during the waiting time, which indicates

Table II. Reported stability constants of copper(II)–lactate complexes (I = 2.0).

Reaction	Log K	Reference
$HL = H^+ + L^-$	–3.81	22
$Cu^{2+} + L^- = CuL^+$	2.45	22
$Cu^{2+} + 2L^- = CuL_2$	4.08	22
$Cu^{2+} + 3L^- = CuL_3^-$	4.70	22
$Cu^{2+} + 2OH^- = Cu(OH)_2$	18.81	24

that the reaction had not reached chemical equilibrium on the titration timescale by traditional burette infusion.

Therefore, we performed "revised pH titration" to ensure sufficient reaction time. We found that the pH values of the solutions allowed to stand for 1 week were highly stable, indicating that the solutions had reached equilibrium. The titration curve produced by the "revised pH titration" method exhibited two equivalence points beyond the HL neutralization point; i.e., $c_{NaOH} = c_{HL}$. Equivalence point (A) was observed at a NaOH concentration ($c_{NaOH} = c_{HL} + c_{Cu(II)}$) of exactly 3.4 M, suggesting that the OH^- reacted with the complexed copper(II) species in a 1:1 Cu(II):OH^- molar ratio. In addition, another equivalence point (B) was observed at $c_{NaOH} = c_{HL} + 2c_{Cu(II)} = 3.8$ M, indicating that an additional fraction of OH^- that corresponds to $c_{Cu(II)}$ also reacted with the copper(II) species in a Cu(II):OH^- molar ratio of 1:1. Interestingly, the final equivalence point using "traditional pH titration" is rather close to (A), while that using the "revised pH titration" method corresponds to (B). Clearly, the "traditional pH titration" method underestimates c_{NaOH} and misses formation about the "hidden" final product, where Cu(II):OH^- = 1:2. The gap between (A) and (B) may be due to the slow rate of shift toward equilibrium, which results in the equilibria for the complexes with Cu(II):OH^- ratios of 1:1 and 1:2 remaining unbalanced within the timescale of the traditional titration method. In contrast, the "revised pH titration", with sufficient equilibrium time, was able to reach equivalence point (B), at $c_{NaOH} = c_{HL} + 2c_{Cu(II)}$, which was hidden using the traditional method.

Here, it is reasonable to consider that $Cu(H_{-1}L)L^-$, $Cu(H_{-1}L)L_2^{2-}$, $Cu(H_{-1}L)_2^{2-}$, and/or $Cu(H_{-1}L)_2L^{3-}$ are formed from the CuL_2 and/or CuL_3^- complexes under alkaline conditions as follows:

$$CuL_2 + OH^- = Cu(H_{-1}L)L^- + H_2O \quad [1.1]$$

$$CuL_3^- + OH^- = Cu(H_{-1}L)L_2^{2-} + H_2O \quad [1.2]$$

$$CuL_2 + 2OH^- = Cu(H_{-1}L)_2^{2-} + 2H_2O \quad [2.1]$$

$$CuL_3^- + 2OH^- = Cu(H_{-1}L)_2L^{3-} + 2H_2O \quad [2.2]$$

$Cu(H_{-1}L)L^-$ and/or $Cu(H_{-1}L)L_2^{2-}$ are the products formed around equivalence point (A), and $Cu(H_{-1}L)_2^{2-}$ and/or $Cu(H_{-1}L)_2L^{3-}$ are those formed around equivalence point (B). In other words, we assume that OH^- participates in complexation by reacting with the α-hydroxyl group of the L^- ligand. Consequently, the existence of equivalence point (A) suggests that the intermediate complexes are $Cu(H_{-1}L)L^-$ and/or $Cu(H_{-1}L)L_2^{2-}$, while equivalence point (B) suggests that the final copper(II)–lactate complexes are $Cu(H_{-1}L)_2^{2-}$ and/or $Cu(H_{-1}L)_2L^{3-}$.

ESI-MS/PESI-MS.—The titration results suggested the existence of $Cu(H_{-1}L)L^-$, $Cu(H_{-1}L)L_2^{2-}$, $Cu(H_{-1}L)_2^{2-}$, and/or $Cu(H_{-1}L)_2L^{3-}$. To obtain direct evidence for the existence of these complexes with the $H_{-1}L^{2-}$ ligand, we used electrospray-ionization mass spectrometry (ESI-MS) in negative-ion mode for the solution at c_{NaOH} = 3.7 M. Under these conditions, only monovalent negative ions are detected, and the values of m/z (where $z = 1$) provide the molecular weights of the anionic species. Notably, signals of species containing one Cu atom were observed as characteristic doublets due to the stable isotopes of Cu (^{63}Cu:^{65}Cu = 100:45), which makes it easy to discriminate the target copper(II) species from the other species present.

Figure 3 shows the mass spectrum obtained as described above, which provides evidence for the presence of $Cu(H_{-1}L)L^-$ in solution. Clusters containing $Cu(H_{-1}L)L^-$ are clearly observed as $[Cu(H_{-1}L)L] \cdot (NaL)^-_x$ (x = 0, 1, 2, and 3) at m/z = 240, 352, 464, and 576, while clusters containing $Cu(H_{-1}L)_2^{2-}$, as $Na[Cu(H_{-1}L)_2] \cdot (NaL)_x^-$ (x = 1, 2, 3, and 4), are observed at m/z = 374, 486, 598, and 710. However, the solution was diluted with water because the ESI-MS method cannot deal with such a highly concentrated solution. Such a dilute solution may contain dissolved species that differ to those in the original bath. In fact, as an example, when the analyte was diluted with water by more than a factor of 1000, $Cu(OH)_2$ was observed to precipitate (see supporting information), indicating that complexes containing the $H_{-1}L^{2-}$ ligand are only stable in concentrated solutions. We therefore sought a technique that did not require dilution for the analysis of the original solution and turned to probe-electrospray-ionization mass spectrometry (PESI-MS).[23]

Compared with conventional ESI-MS, the PESI-MS method exhibits improved accuracies and measurement limitations for the analyses of highly-concentrated aqueous solutions, which is achieved by downsizing the electrospray emitter; i.e., by replacing the 200-μm-diameter capillary with a fine needle with a diameter of 0.7 μm. In this study, PESI-MS was operated in positive-ion mode. Therefore, only ionic groups that bear single positive charges can be observed, and the values of m/z provide the molecular weights of the ionic species.

Figure 4 displays the PESI-MS spectrum obtained for the undiluted 0.4 M aqueous copper(II)–3.0 M lactate solution at c_{NaOH} = 3.7 M. Clusters containing $Cu(H_{-1}L)_2^{2-}$ are clearly observed as $Na_3[Cu(H_{-1}L)_2] \cdot (NaL)_x^+$ (x = 1, 2, 3. . .) at m/z = 308, 420, 532, and so on. In positive-ion mode, however, clusters containing $Cu(H_{-1}L)L^-$ are not clearly observed by PESI-MS, despite ESI-MS evidence indicating their existence. The absence of $Cu(H_{-1}L)L^-$-containing clusters may be ascribable to the inability of $Cu(H_{-1}L)L^-$ to form monovalent positive-ion clusters for some reason. We have also attempted to operate PESI-MS in negative-ion mode; however corona discharges were observed during the electrospray process and the samples failed to ionize.

Consequently, through the use of ESI-MS and PESI-MS, clusters containing $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ were observed, which indicate that among $Cu(H_{-1}L)L^-$, $Cu(H_{-1}L)L_2^{2-}$, $Cu(H_{-1}L)_2^{2-}$, and $Cu(H_{-1}L)_2L^{3-}$, namely the undetermined-complex candidates suggested by the titration experiments, $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ are plausible complexes that exist in solution. It is important to note that $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ are only stable under alkaline conditions in highly concentrated solutions of copper(II)-lactate complexes. In addition, almost all clusters that contain $H_{-1}L^{2-}$ are clusters of copper(II)–lactate complexes. Hence, no free $H_{-1}L^{2-}$ was observed by mass spectrometry, which is in agreement with the pH-titration results that indicate that only when complexed to Cu(II) can the α-hydroxyl group of L^- become deprotonated. The pKa of such an α-hydroxyl group is empirically considered to be above 13. It is reasonable to believe that no $H_{-1}L^{2-}$ is formed from the deprotonation of free L^- ions even under the alkaline conditions. Therefore, deprotonation of the α-hydroxyl group of the coordinated L^- ions may be due to the strong Lewis acidity of the copper(II) ions, especially in a concentrated solution with a relatively high ionic strength.

General discussion on the dissolved species: questions regarding previously reported copper(II) lactate complexes.—The high concentration appears to be the key reason why copper(II)-$H_{-1}L^{2-}$ complexes have remained undetermined under alkaline conditions. Usually, researchers use thermodynamic data to predict stable species in aqueous solutions; these data are based on low concentrations and low ionic strengths. On the other hand, the Cu_2O electrodeposition

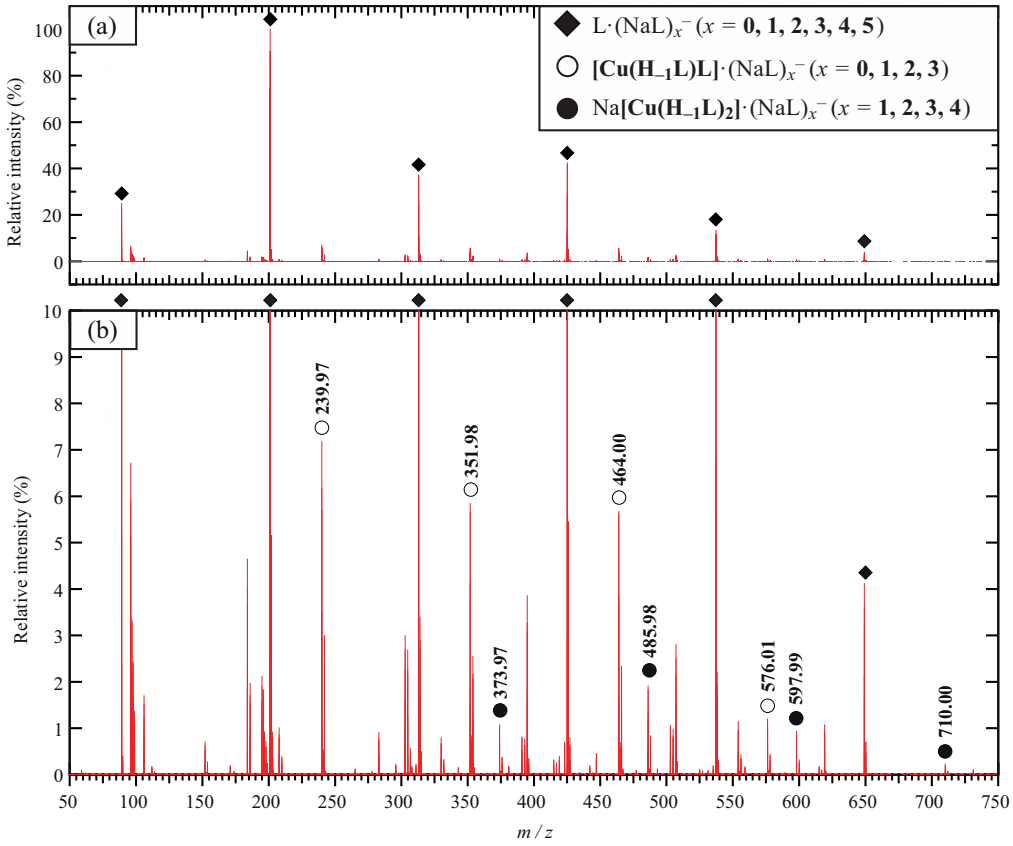

Figure 3. (a) Full and (b) enlarged ESI-MS spectra of a 1000-fold-diluted supernatant aqueous solution of 0.4 M copper(II)–3.0 M lactate at c_{NaOH} = 3.7 M.

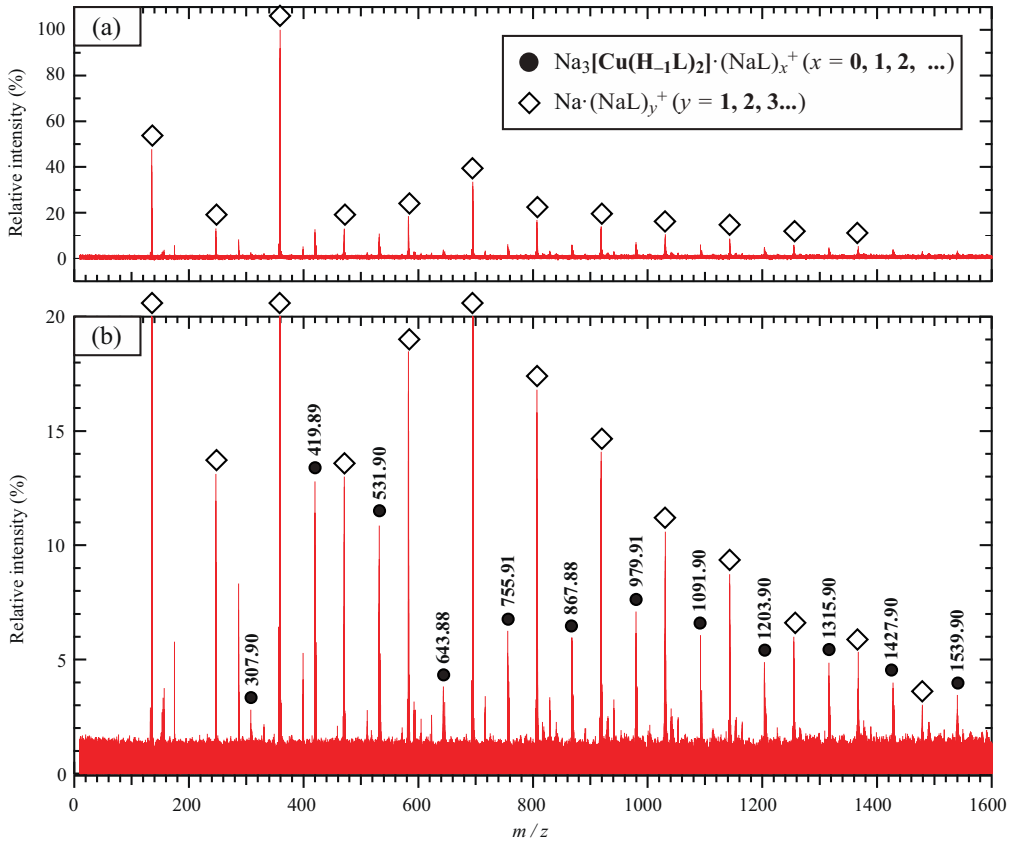

Figure 4. (a) Full and (b) enlarged PESI-MS spectra of an aqueous solution of 0.4 M copper(II)–3.0 M lactate at c_{NaOH} = 3.7 M, acquired without sample dilution.

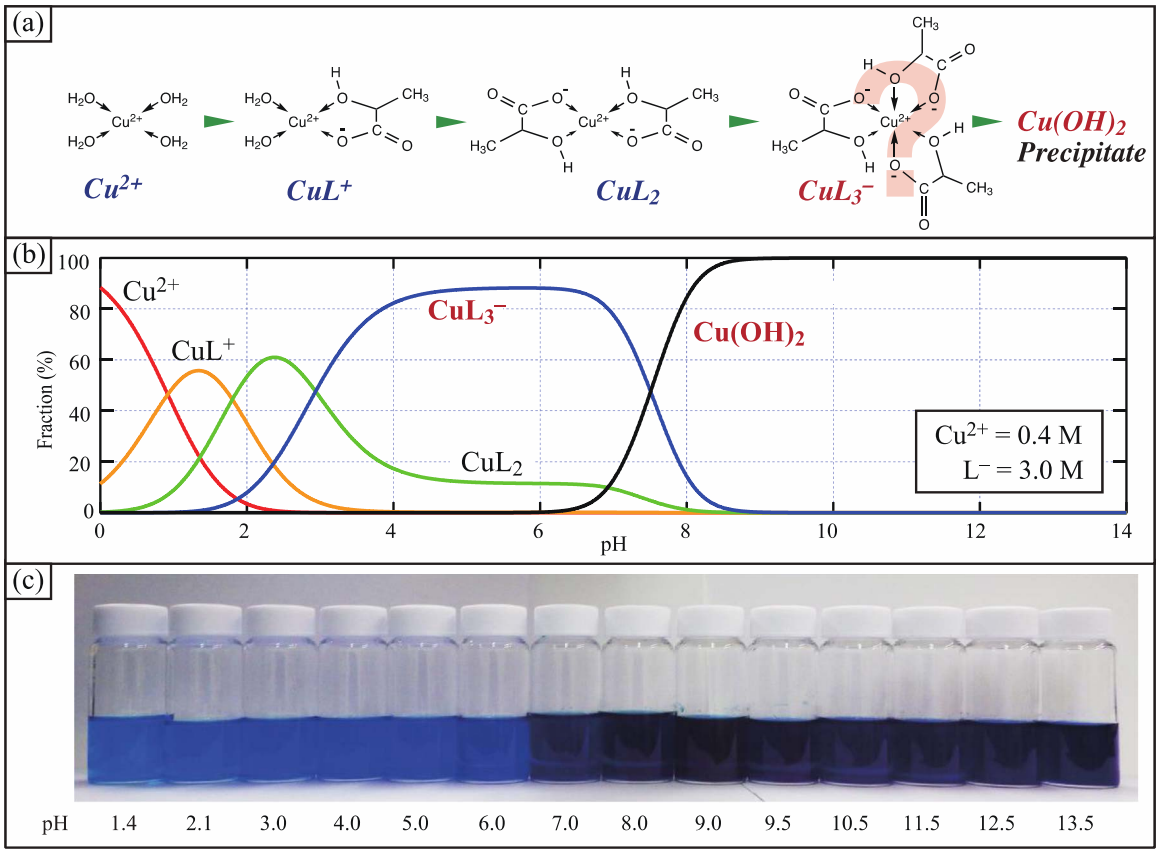

Figure 5. (a) Structure and (b) pH-speciation diagram of the "theoretically stable" copper(II) species in 0.4 M copper(II)–3.0 M lactate solutions, based on reported thermodynamic data.[22,24] (c) Photographic images of actual 0.4 M copper(II)–3.0 M lactate solutions in the 1.4–13.5 pH range, in which the color of the solution changed, but no precipitation was observed.

bath is a highly concentrated solution; for example, it contains large amounts of lactate ions (L^-), alkali-metal ions, and hydroxide ions at a high ionic strength I of 4.3 at pH 12.5. In addition, the dissolved species and/or chemical equilibria are different to those predicted by thermodynamic calculations at different concentrations and ionic strengths.

Figure 5a shows a schematic diagram, and Figure 5b shows a pH-speciation diagram, of copper(II)–lactate complexes, constructed using reported thermodynamic data, namely the acid dissociation constants of HL and the stability constants of the copper(II) lactate complexes, CuL^+, CuL_2, CuL_3^-, and $Cu(OH)_2$ precipitate (Table II).[22,24] The first problem encountered is the presence of CuL_3^-. It is reasonable to propose that CuL_3^- is a six-coordinate regular octahedral complex with D_3 symmetry, in which L^- acts as a bidentate ligand. It is known, however, that a Jahn–Teller d^9 Cu(II) ion has a tendency to form a square planar or square (bi)pyramidal complex rather than a regular octahedrally coordinated species. In fact, the central Cu(II) of CuL_3^-, if present, has 21 valence electrons, which not satisfies the empirical 18-electron rule. Therefore, we question the existence of CuL_3^-. The ESI-MS spectrum (Figure 3) exhibited a signal assignable to CuL_3^- at $m/z = 330$, but its intensity was very weak compared to those corresponding to the $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$-containing species.

Another question surrounds the precipitation of $Cu(OH)_2$, which is predicted from the thermodynamic data. The pH speciation diagram shown in Figure 5b indicates that $Cu(OH)_2$ precipitates at pH values in excess of ~8.0. However, the photographic images of a set of highly-concentrated copper(II)–lactate solutions (Figure 5c), prepared for the "revised pH titration" method, do not reveal any precipitation, even at pH = 13.5. This suggests that all copper(II) ions are coordinated by L^- and/or $H_{-1}L^{2-}$, which prevent these ions from forming $Cu(OH)_2$. The absence of any $Cu(OH)_2$ precipitation renders the electrodeposition Cu_2O possible, as reported previously. Hence, the known thermodynamic data, which were acquired at low concentrations, are not useful for predicting the actual chemical species present in these highly concentrated solutions.

Prior to this work, research aimed at elucidating the unknown copper(II)–lactate complexes had been reported on two occasions. Leopold et al. assumed that the copper(II)–lactate system behaved in a similar fashion to the copper(II)–tartrate system, and suggested that the dominant complex in the alkaline copper(II)–lactate solution is $Cu(H_{-1}L)_2^{2-}$ (Note that $H_{-1}L^{2-}$ ion is described as L^{2-} in Ref. 18) by analogy with the deprotonated $Cu(H_{-1}T)_2^{4-}$ complex ($H_{-1}T^{3-}$; $^-OOCCH(OH)CH(O^-)COO^-$) in the copper(II)–tartrate solution.[18] They also suggested the existence of $Cu(H_{-1}L)_2(OH)^{3-}$ on the basis of a pH-titration experiment at pH > 8, since the copper(II), i.e., the assumed $Cu(H_{-1}L)_2^{2-}$, was observed to react with OH^- with an approximately 1:1 Cu(II):OH^- ratio.[18] Recently, Achilli et al. used energy-dispersive X-ray absorption spectroscopy (EDXAS) to analyze the dissolved copper(II)–lactate complex under alkaline conditions. They concluded that the central copper(II) (bearing the oxygen atoms) is four coordinated.[19] Furthermore, according to their structure-model fitting, CuL_4^{2-} is more likely to be the dissolved copper(II)–lactate complex, assuming that excess L^- acts as a monodentate ligand, rather than a bidentate ligand. They did not discuss the possibility of α-hydroxyl-group deprotonate to form $H_{-1}L^{2-}$ from L^-.

Both previous reports (Leopold et al. and Achilli et al.) did not discuss the effect of complexation time. Actually, the pH-titration curve in the report of Leopold[18] is similar to that obtained in the "traditional pH titration" experiment reported herein, in which only

one equivalence point was observed at pH > 8 without buffering. It is important to note that Leopold et al. only conducted pH-titration experiments at pH > 8 and assumed that $Cu(H_{-1}L)_2(OH)^{3-}$ is the final complex. In this case, the complexation reaction between copper(II) aquo ions and HL is: $Cu^{2+} + 2HL + 5OH^- = Cu(H_{-1}L)_2(OH)^{3-} + 4H_2O$, where Cu(II):$OH^-$ = 1:5, indicating that five equivalents of OH^- is required. In contrast to these studies, we analyzed alkaline copper(II)–lactate solutions over the full pH range after a sufficient reaction time, and confirmed that only four equivalents of OH^- is required to form the final complex from copper(II) aquo ions and HL. Moreover, we directly observed $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ in ESI-MS and PESI-MS experiments for the first time. Notably, as opposed to the previously proposed complexes, namely $Cu(H_{-1}L)_2(OH)^{3-}$ and CuL_4^{2-}, the currently proposed complexes, namely $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$, are not only square-planar coordinated, but they also satisfy the 18-electron rule (17 valence electrons).

Isosbestic points by UV-Vis spectroscopy.—UV-Vis spectroscopy was used to determine the complexation equilibria of the copper(II)–lactate complexes. Figure 6 displays the UV-Vis absorption spectra acquired over the 0.7–12.8 pH range, which can be subdivided into three groups.

In region I (Figure 6b), in which c_{NaOH} ranges from 0 to c_{HL}, a slight blue shift in the copper(II) *d-d* transition is observed, which indicates a change in the complexation of the ligand with copper(II). No isosbestic point is observed in this range, but the absorbance, i.e., the absorption cross-section, increases with increasing pH. Based on these observation and previously reported thermodynamic data,[22] we assume that the copper(II)–lactate complexes in region I involve hydrated Cu^{2+}, i.e., $[Cu(H_2O)_4]^{2+}$, CuL^+, i.e., $[CuL(H_2O)_2]^+$, and CuL_2.

Region II (Figure 6c), in which $c_{HL} < c_{NaOH} < c_{HL} + c_{Cu(II)}$, the spectra exhibit large blue shifts with increasing pH, which reveal that the complexation regime involving the ligand field around the copper(II) changes further. Here, OH^- ions begin to react with the copper(II)–lactate complexes, i.e., CuL_2, in a 1:1 Cu(II):OH^- ratio to form a new complex. In addition, an isosbestic point is observed at approximately 746 nm, indicating that only two optically active copper(II)-containing species are in equilibrium. Based on the titration and the ESI-MS/PESI-MS results, we propose that the two copper(II)–lactate complexes are CuL_2 and $Cu(H_{-1}L)L^-$. Therefore, in region II, complexation proceeds as follows:

$$CuL_2 + OH^- = Cu(H_{-1}L)L^- + H_2O \quad [3]$$

When region II is complete, at $c_{NaOH} = c_{HL} + c_{Cu(II)}$, almost all the CuL_2 has transformed to $Cu(H_{-1}L)L^-$ through deprotonation of the α-hydroxyl group.

Region III (Figure 6d) consists of two parts. In the $c_{NaOH} = c_{HL} + c_{Cu(II)}$ to $c_{NaOH} = c_{HL} + 2c_{Cu(II)}$ range, the spectra exhibit further blue shifts, indicating that the ligands are still changing. Another set of isosbestic points are observed at approximately 460 nm and 599 nm, indicating that there are only two chemical species in equilibrium, which differ from CuL_2 and $Cu(H_{-1}L)L^-$. The second part of this region corresponds to $c_{NaOH} > c_{HL} + 2c_{Cu(II)}$. In this part, the absorption spectra overlap and hardly change with increasing pH. Therefore, the UV-Vis results clarify that $Cu(H_{-1}L)_2^{2-}$ is the final product, and supported the conclusions made on the basis of the titration results. The chemical equilibrium in region III is:

$$Cu(H_{-1}L)L^- + OH^- = Cu(H_{-1}L)_2^{2-} + H_2O \quad [4]$$

The L^- moiety of $Cu(H_{-1}L)L^-$ changes during deprotonation of the α-hydroxyl group to form $Cu(H_{-1}L)_2^{2-}$.

We finalized the complexation reactions in concentrated copper(II)–lactate solutions under neutral and alkaline conditions by UV-Vis spectroscopy. The observation of isosbestic points in regions II and III confirm that no other stepwise complexes apart from CuL_2, $Cu(H_{-1}L)L^-$, and $Cu(H_{-1}L)_2^{2-}$ (*e.g.*, $Cu(H_{-1}L)_2(OH)^{3-}$ or CuL_4^{2-}) exists in these regions. In addition, since the absorption spectra did not change at pH values in excess of 12.4, we conclude that $Cu(H_{-1}L)_2^{2-}$ is the final product. To summarize, we provide a revised schematic diagram for dissolved copper(II)–lactate complexes in Figure 7. It turns out that $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ are the dissolved complexes in the pH 9.0–9.5 range, while only $Cu(H_{-1}L)_2^{2-}$ exists in the pH 12.0–12.5 range, which suggests that the pH dependence of the Cu_2O orientation during electrodeposition[13–17] is the result of changes in the complexes present in solution.

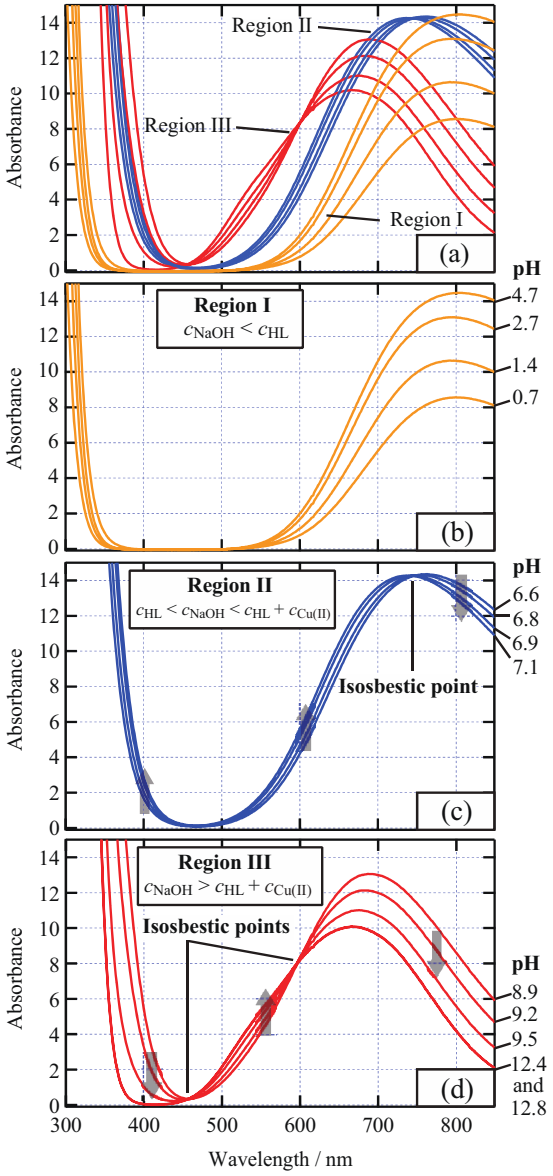

Figure 6. (a) UV-Vis absorption spectra of aqueous 0.4 M copper(II)–3.0 M lactate solutions over the full pH region, which can be divided into: (b) Region I ($c_{NaOH} < c_{HL}$), (c) Region II ($c_{HL} < c_{NaOH} < c_{Cu(II)} + c_{HL}$), and (d) Region III ($c_{NaOH} > c_{Cu(II)} + c_{HL}$). The arrows indicate the direction of spectral changes upon pH increase.

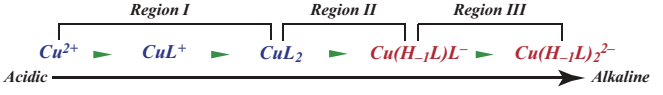

Figure 7. Revised schematic diagram for copper(II)–lactate complexes dissolved in highly concentrated aqueous solutions based on this work.

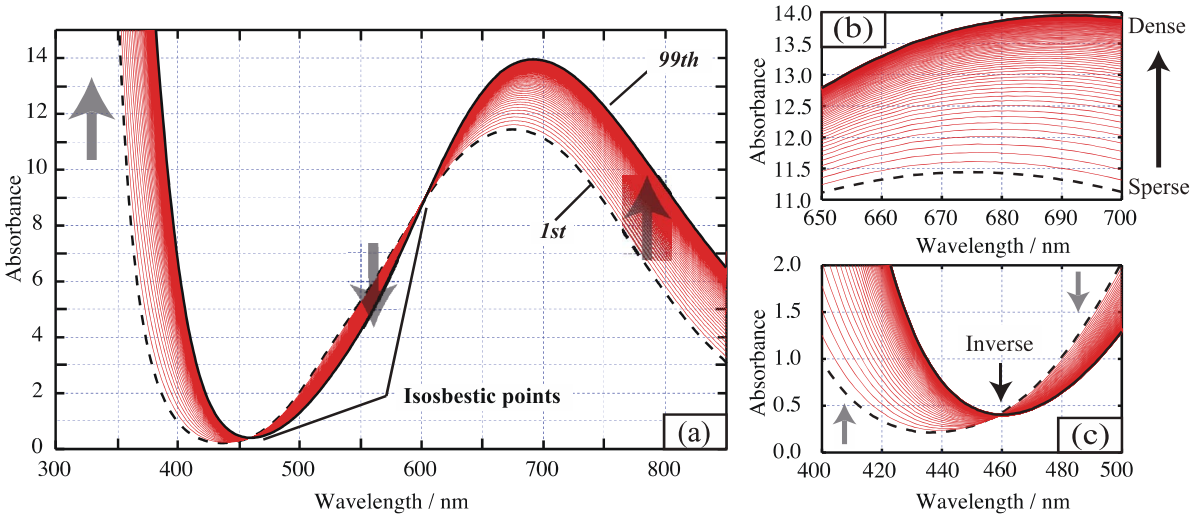

Figure 8. (a) Full UV-Vis absorption spectra of a 0.4 M copper(II)–3.0 M lactate solution with 3.7 M NaOH ($c_{NaOH} = c_{HL} + 1.75c_{Cu(II)}$) as functions of time. (b) The enlarged view clearly shows increasing spectral density with time, which indicates a decrease in reaction rate. (c) Inverting the change in spectral direction reveals the existence of isosbestic points, which are the same as those observed for Region III (see text for details).

The effect of complexation time.—We also used UV-Vis spectroscopy to determine the time required for $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ to equilibrate. Figure 8 displays the temporal change in the UV-Vis absorption spectrum of a 0.4 M copper(II)–3.0 M lactate solution with 3.7 M NaOH ($c_{NaOH} = c_{HL} + 1.75c_{Cu(II)}$), which is within Region III where both $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$ exist. We focused on this solution because the equilibrium time varies with OH^- concentration and the solution provides a suitable timeframe for experimental detection. Measurements began soon after the copper(II)–lactate solution was mixed with NaOH, and finished 24 h later, after the 99th measurement; consequently the time between each measurement is about 15 min. This experiment reveals that the UV-Vis absorption spectrum changes significantly over time, and indicates that the two dissolved complexes require at least 24 h to equilibrate. The concentration of $Cu(H_{-1}L)_2^{2-}$ was observed to decrease with time, while that for $Cu(H_{-1}L)L^-$ increased through a shift in equilibrium. In addition, a set of isosbestic points were observed at the same wavelengths as those observed in Region III, namely at about 460 nm and 599 nm, which confirms the presence of $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$.

Conclusions

We reveal copper(II)–lactate and copper(II)–lactate-derived complexes in highly concentrated alkaline solutions. These solutions are used to fabricate low-cost Cu_2O thin films by electrodeposition. The complexes contain doubly deprotonated lactate ions as ligands, namely $Cu(H_{-1}L)L^-$ and $Cu(H_{-1}L)_2^{2-}$, and the difference of dissolved complexes seem contribute to the pH dependence of the Cu_2O orientation. $H_{-1}L^{2-}$ coordinated to copper(II) ions has not been previously experimentally observed, which we report for the first time through pH titration, ESI-MS/PESI-MS, and UV-Vis spectroscopy. In highly concentrated alkaline solutions, the $H_{-1}L^{2-}$ ligand, which appears to be stable only through coordination to copper(II), provides new insight into coordination chemistry. Moreover, deprotonation of the α-hydroxyl group can take place in a similar manner to carboxylic acids, such as glycolic acid, to function as a ligand in highly concentrated alkaline solutions.

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